INTRODUCTION

This report summarizes the work performed under NASA EPSCoR Grant NAGW 4414 "Nebraska Center for Space Communications Research", at the University of Nebraska -Lincoln, Department of Electrical Engineering and the Center for Microelectronic and Optical Materials Research. from April 1, 1995 to March 31, 1996. This progrm consists of two projects: deposition and characerization of materials and material systems that are conductive enough to dissipate surface charge that accumulates during low earth orbit, resistant to atomic oxygen attack, protective of underlying materials from atomic oxygen, transparent to ultraviolet light, and can serve as anti reflecting coatings with respect to the solar spectrum, and to develop a photochromic material for space applications whose infrared emissivity changes in response to solar radiation.

OXIDATION RESISTANT COATINGS

I. Introduction

A list of the specific materials properties of interest for oxidation resistant coatings are given in Table I. Based on our previous work we have focused on the deposition of AlN, and doped AlN films Our program has demonstrated that these materials systems can met the requirements outlined in Table I.

II. Deposition System

The deposition system was specifically constructed for this project. The vacuum chamber consists of an oil diffusion pumped stainless steel belljar with a base pressure below 2×10^{-6} Torr. A single dc magnetron sputter gun is located in the center of the chamber and pointing up. The sputtering gas, in this case argon, is injected directly into the gap between the ground shield and target, where the ground shield is fitted with a stack that helps confine the injected gas to the target region. The substrate holder is approximately 12 cm distant from the surface of the target, and a reactive gas injection ring is located directly on front of the substrate. A shutter is placed between the ring and substrate holder.

The combination of gas injection into the gun, the stack, and the reactive gas injection ring near the substrate allows relatively low gas flows to establish operating pressures. This in turn, allows the diffusion pump to be kept wide open during deposition, providing a low overall chamber pressure, which is less than 2 mTorr. This improves the deposition.

III. Aluminum Nitride

Aluminum nitride was deposited by dc magnetron sputtering from a pure aluminum target in a Ar/N_2 atmosphere. The reaction that forms AlN should occur at the depositing film surface, thus control over the deposition conditions may provide composition control. The substrates were single crystal silicon, or fused quartz disks. A range of gas flow ratios and subsrates were explored, where it was found that stooichuiometric AlN could be easily deposited from a barietyu of conditions. A typical Auger scan after removal of the surface layer is seen in shows that virtually all films deposited in this system had an oxygen content of a few percent or less. The film composition was determined by measuring the peak to peak height of each signal and applying the standard Auger sensitivity factors. Transmission and reflection data were used to determine the band gap which is on the order of 4.0 eV for all films with nitrogen/aluminum ratios close to 1.

Upon ashing in the contamination free asher, the transmittance was unchanged for an active oxygen fluence of 8×10^{20} cm^{-2}.

IV. Resistivity

The resistivity of the aluminum nitride films was determined by depositing the material on circular quartz disks, or through a circular shadow mask onto a SiO_2 coated silicon wafer. Aluminum contact pads were sputtered through a shadow mask in a square pattern onto the edge of the film. The current was passed through 2 adjacent contacts and voltage was read across the remaining adjacent contacts. This is the van der Pauw configuration, where the resistivity can be calculated from:

$$\rho = (\pi t V)/[I(\ln 2)]$$

where t is the film thickness, V is the voltage, and I is the current.

Based on the system used we could measure resistivity on the order of 10^8 Ω-cm or less. All AlN films tested were greater than this value.

The initial goal in this work was to sputter deposit AlGaN alloys of appropriate composition in order to develop a film of appropriate resistivity. This approach called for a single Al_xGa_{1-x} target, with an appropriate

value of x. Unfortunately, a manufacturer could not be located that would fabricate such a target. Future work will focus on dual target sputtering from an Al target and GaN target to deposit these films.

In view of this development, we have focused on alternate approach to depositing films with the appropriate resistivity. Aluminum nitride can be doped with silicon, yielding an n-type semiconductor. Furthermore Al/Si alloy sputtering targets are commercially available. We have obtained a 1%Si/Al (by weight) target and a 5%Si/Al (by weight) target. Although the results are only preliminary, films made from the 1% target have a resistivity on the order of 10^6 ohm-cm, at least a 2 order of magnitude drop from films madew withoutsilicon, and the films made from the 5% target are on the order of
10^5 ohm-cm. This process has not been optimized with respect to resistivity, and further improvement are anticipated.

PHOTOCHROMIC MATERIALS

The objective of this work was to develop a photochromic material for space applications whose infrared emissivity changes in response to solar radiation. Some photochromic materials that are useful for optical and electronic applications fail in practical use because of their lack of thermal stability and light fatigue resistance. To achieve the research goal, we used the sol-gel coating technique to dope an organic photochromic material into several robust matrices. The robust matrices are metal alkoxide, metal alkoxide-polymer, and pure polymer materials.

The organic doping of metal alkoxide materials was done by sol-gel processing because it is an inexpensive way to produce thin and thick films without cracking. This can be attributed to an increased relaxation of these materials, caused by various mechanisms such as hydrolysis and polycondensation. The second matrix was made by the incorporation of metal alkoxides into organic polymeric materials via the in-situ polymerization of the oxides by sol-gel processing. This process is a way to promote compatibility between the inorganic network and the organic polymeric material. The pure polymeric materials used for the third matrix were selected to be stable at high temperatures.

The films on silicon and quartz substrates were examined, with and without ultraviolet (UV) light irradiation, by ellipsometry, ultaraviolet/visible/near-infrared transmission spectroscopy, and Fourier Transform Infrared (FTIR) spectroscopy. The UV light intensity was adjusted to simulate the solar spectrum. Ellipsometry is based on the polarization change of light upon reflection from a sample surface, and determines optical constants and thicknesses. The ellipsometric data were obtained by using a variable angle of incidence spectroscopic ellipsometer (VASE) and analyzed with a WVASE 32 program. The Cauchy model and Cauchy-Lorentz combined model were used to fit the unirradiated and irradiated films, respectively. The best results were obtained with spiropyran doped films. The spiropyran doping into the metal alkoxide matrix destroyed the photochromism of the dopant. However, spiropyran doping into the metal alkoxide-polymer and the pure polymer matrices produced a change in the extinction coefficient with UV light irradiation. This means that the absorption coefficient and hence the emissivity of the films is being modulated with UV light. The calculated thicknesses of the films were in the range of 2 to 6 microns.

Infrared spectroscopy has long been a sensitive analytical technique for elucidation of molecular structure of both inorganic and organic compounds. The FTIR spectra of samples, with or without UV light irradiation, were obtained by using a Bomem Michelson series MB 100 FTIR spectrometer. It has been reported that spiropyran compounds show photochromism which results from changes between the spiropyran form and the merocyanine form with C=C double bond conjugation. Upon bond cleavage, the closed spiropyran molecule converts to an open and colored merocyanine dye. This conversion of spiropyran to merocyanine under a UV lamp is the key factor in this research since it causes changes in the IR spectrum as well as the visible spectrum. In the FTIR spectra of several spiropyran doped matrix materials, two spectral regions (6-7 μm and 7.5-8.5 μm) were examined for the spiropyran bond opening. The transmission ratio for the irradiated to unirradiated samples reached about 24% at a particular IR wavelength. High temperature stable polymer materials such as polyimide derivatives were used as a matrix material for this sample. Further study of these materials is needed because their preparation is very difficult.

In conclusion, we have achieved the objective of modulating IR transmitance, and thus the emissivity, of films with spiropyran dopants. In particular, wide band modulation from 6 to 15 μm was realized with specific wavelengths reaching transmittance changes of about 24%. An abstract based on this work, "Synthesis and

Spectroscopic Analysis of Infrared Photochromic Materials" has been submitted to the Fall 1996 Materials Research Society meeting. We will also be submitting a journal article this Fall, and subsequently submitting a reprint to NASA. For space applications the robustness of the materials needs to be tested, and possibly further work needs to be done to achieve space-compatible materials. To make robust matrices, we have used a polymerization process to incorporate inorganic oxides into organic polymeric materials and we have used pure polymer materials. We have also begun another approach using an aromatic pure polymer matrix which is stable at high temperatures, in this case a polyimide derivative. In the contract period we were only able to make one of the polyimide derivative films, so much more work is required in this area.